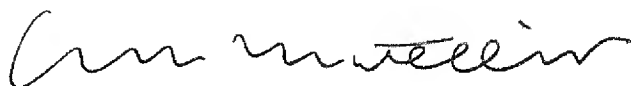


I, Yoshiyuki Matsushima, a patent attorney of HATORI & CO., AKASAKA HKN  
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sincerely declare that I well understand the English and Japanese languages and that  
the attached English translation is a correct, true and faithful translation of the  
Japanese priority document of

Japanese Patent Application No. 2004-319789 filed on November 2, 2004

to the best of my knowledge.

Date : 2009. 10. 19



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Claims 1

Specification 1

Drawings 1

Abstract 1

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[Document Name] CLAIMS

[Claim 1]

5 An electrode for nonaqueous electrolyte secondary batteries characterized by having an output terminal attached to a surface of the electrode at a position corresponding to a position, in viewing along the thickness direction of the electrode, where an active material layer exists.

[Claim 2]

10 The electrode for nonaqueous electrolyte secondary batteries according to claim 1, wherein an active material contained the active material layer comprises a material having low electroconductivity.

[Claim 3]

15 The electrode for nonaqueous electrolyte secondary batteries according to claim 1 or 2, comprising a pair of current collecting surface layers and at least one active material layer interposed between the surface layers, the surface of each of the surface layers being adapted to be brought into contact with an electrolyte, the active material layer containing a particulate active material having high capability of forming a lithium compound, wherein the output terminal is attached to the surface of the current collecting surface layer.

[Claim 4]

20 The electrode for nonaqueous electrolyte secondary batteries according to claim 3, wherein a material which constitutes the current collecting surface layer penetrates the thickness direction of the active material layer to provide an electrical connection between the two surfaces of the electrode such that the electrode has a current collecting function as a whole.

25 [Claim 5]

The electrode for nonaqueous electrolyte secondary batteries according to claim 3 or 4, wherein the surface layers each have a thickness of 0.3 to 10  $\mu\text{m}$ .

[Claim 6]

30 The electrode for nonaqueous electrolyte secondary batteries according to claim 3, wherein the surface layer has micropores extending in the thickness direction

thereof, the micropores being configured to allow a nonaqueous electrolyte to penetrate therethrough.

[Claim 7]

5 The electrode for nonaqueous electrolyte secondary batteries according to claim 6, wherein the micropores lead to the active material layer, the micropores of at least one of the surface layers have an average open area of 0.1 to 50  $\mu\text{m}^2$  and an open area ratio of 0.1% to 20%, and a thick conductor for current collection is absent from the electrode.

[Claim 8]

10 The electrode for nonaqueous electrolyte secondary batteries according to any one of claims 3 to 7, wherein the surface layers are formed by electroplating.

[Claim 9]

15 The electrode for nonaqueous electrolyte secondary batteries according to any one of claims 3 to 8, wherein each of the surface layers contains a metal material having low capability of forming a lithium compound.

[Claim 10]

The electrode for nonaqueous electrolyte secondary batteries according to any one of claims 3 to 12, wherein the particulate active material comprises particles of a silicon material or particles of a tin material.

20 [Claim 11]

The electrode for nonaqueous electrolyte secondary batteries according to claim 3, wherein the electrode further comprises an electroconductive metal foil in the middle of the thickness direction thereof as a core, the active material layer is present on both sides of the metal foil, the current collecting surface layers are each adjacent to the  
25 respective active material layers, and the total thickness of the electrode is 10 to 100  $\mu\text{m}$ .

[Claim 12]

The electrode for nonaqueous electrolyte secondary batteries according to any one of claims 1 to 14, which is a negative electrode.

## [Claim 13]

A process of producing the electrode for nonaqueous electrolyte secondary batteries according to claim 3, the process comprising the steps of:

- 5     applying an electroconductive slurry containing a particulate active material to a carrier foil to form an active material layer,
- immersing the carrier foil with the active material layer in a plating bath to conduct electroplating to form a surface layer on both sides of the active material layer,
- peeling the carrier foil off one of the surface layers to obtain an electrode, and
- attaching an output terminal to one of the surface layers.

## 10   [Claim 14]

A process of producing the electrode for nonaqueous electrolyte secondary batteries according to claim 3, the process comprising the steps of:

- electroplating one side of a carrier foil to form a first current collecting surface layer,
- 15     applying an electroconductive slurry containing a particulate active material to the first surface layer to form an active material layer on the active material layer,
- electroplating the active material layer to form a second current collecting surface layer on the active material layer,
- peeling the carrier foil off the first current collecting surface layer to obtain an
- 20     electrode, and
- attaching an output terminal to one of the current collecting surface layers.

## [Claim 15]

- The process according to claim 14, further comprising forming a coat of a material different from the material constituting the first current collecting surface layer
- 25     on the one surface of the carrier foil to a thickness of 0.001 to 1  $\mu\text{m}$  before forming the first current collecting surface layer.

[Document Name] DESCRIPTION

[Title of Invention] ELECTRODE FOR NONAQUEOUS ELECTROLYTE  
SECONDARY BATTERY

[Technical Field]

5 [0001]

This invention relates to an electrode for nonaqueous electrolyte secondary batteries such as lithium ion secondary batteries and a process of producing the same.

[Background Art]

[0002]

10 In the manufacture of electrodes for lithium ion secondary batteries, it has been a commonly followed practice to, as illustrated in Fig. 4, apply an active material to a surface of a current collector 100 with spacing to make active material-coated regions 101 and uncoated regions 102 and to attach a current collecting tab 103 to each uncoated regions 102 (see, e.g., Patent Document 1 ).

15 [0003]

[Patent Document 1] JP-A-11-354110

[Disclosure of the Invention]

[Technical Problem]

[0004]

20 The intermittent application as referred to above makes the electrode production process complicated. The attachment of the current collecting tabs must be controlled accurately to successfully place each tab in each uncoated region, which also makes the process complicated. In addition, the uncoated regions are, in other words, active material-deficient regions, which means a corresponding loss of capacity.

25 [0005]

Accordingly, an object of the present invention is to provide an electrode for nonaqueous electrolyte secondary batteries that is free from the above-mentioned various disadvantages of conventional techniques.

[Solution to Problem]

[0006]

The present invention achieves the above object by the provision of an electrode for nonaqueous electrolyte secondary batteries characterized by having an output terminal attached to a surface of the electrode at a position corresponding to a position, in viewing along the thickness direction of the electrode, where an active material layer exists.

[0007]

The invention also provides a preferred process of producing the electrode. The process for non aqueous electrolyte secondary batteries, comprising the steps of applying an electroconductive slurry containing a particulate active material to a carrier foil to form an active material layer, electroplating the carrier foil having the active material layer by immersing in a plating bath to form a current collecting surface layer on both sides of the active material layer, peeling the carrier foil off one of the current collecting surface layers to provide an electrode, and attaching an output terminal to either of the current collecting surface layers.

[0008]

The present invention also provides another preferred process of producing the electrode. The process for non aqueous electrolyte secondary batteries, comprising the steps of electroplating one surface of a carrier foil to form a first current collecting surface layer, applying an electroconductive slurry containing a particulate active material to the first surface layer to form an active material layer, electroplating the active material layer to form a second current collecting surface layer on the active material layer, peeling the carrier foil off the first current collecting surface layer to provide an electrode, and attaching an output terminal to either of the first and second current collecting surface layers.

[Advantageous Effects of the Invention]

[0009]

The electrode for nonaqueous electrolyte secondary batteries of the present invention has a place in itself to attach an output terminal. It is no more necessary to provide an active material-deficient region that has been required for the attachment of an output terminal. As a result, the electrode has an accordingly increased capacity. No need to provide an active material-deficient region brings about simplification of the production process. The output terminal can be directly attached to the surface of the

electrode with no particular positional restriction, which also makes the production process simpler.

[The Best Mode for Carrying out the Invention]

[0010]

5       The present invention will be described based on its preferred embodiments with reference to the accompanying drawings. These embodiments represent application of the present invention to a negative electrode of nonaqueous electrolyte secondary batteries. Fig. 1 schematically illustrates an enlarged essential part of a first embodiment of the invention. While only one side of the negative electrode is  
10 illustrated, the other side has almost the same structure as shown in Fig. 1.

[0011]

      The negative electrode of the first embodiment has a first surface 1 (shown) and a second surface (not shown). The negative electrode 10 has, between the two surfaces, an active material layer 3 containing a particulate active material 2 having  
15 high capability of forming a lithium compound. Each side of the active material layer 3 is continuously covered with a current collecting surface layer 4 (only one of the surface layers 4 is shown). The surface layers 4 on both sides are inclusive of the first surface 1 and the second surface, respectively. As is understood from Fig. 1, the negative electrode 10 does not have such a thick conductor for current collection, called  
20 a current collector, e.g., metal foil or expanded metal, as has been used in conventional negative electrodes.

[0012]

      The surface layers 4 are adapted to be brought into contact with a nonaqueous electrolyte when the negative electrode 10 is assembled into a battery. The surface  
25 layers 4 participate in the electrode reaction. In other words, the nonaqueous electrolyte passes through the surface layer 4 along the thickness direction thereof. In contrast, a thick, current-collecting conductor used in a conventional negative electrode has no surface in contact with an electrolyte when it has an active material layer on its both sides. The current-collecting conductor does not participate in the electrode  
30 reaction. Alternatively, when it has an active material layer on one side thereof only one surface is in contact with an electrolyte. In addition, the nonaqueous electrolyte passes through the current-collecting conductor. In other words, in the absence of a thick, current-collecting conductor, the surface layers 4, i.e., the outermost layers of the negative electrode participate in the passage of an electrolyte and also bears a current



collecting function combined with a function for preventing fall-off of the active material.

[0013]

As stated above, the surface layers 4 have a current collecting function. They  
5 also serve to prevent the active material of the active material layer 3 from falling off  
due to expansion and contraction accompanying intercalation and deintercalation of  
lithium. The surface layers 4 are made of a metal that can be a current collector of  
nonaqueous electrolyte secondary batteries, preferably a metal that can be a current  
collector of lithium ion secondary batteries. Such metals include metal materials  
10 having low capability of forming a lithium compound, such as copper, nickel, iron,  
cobalt, and alloys thereof. It is particularly convenient to use copper, nickel, and their  
alloys. Nickel is preferred for giving an increased strength to the negative electrode 10.  
A nickel-tungsten alloy is especially preferred to form high-strength surface layers 4.  
The two surface layers 4 may be of the same or different materials. The expression  
15 "low capability of forming a lithium compound" as used herein means no capability of  
forming an intermetallic compound or a solid solution with lithium or, if any, the  
capability is such that the resulting lithium compound contains only a trace amount of  
lithium or is very labile.

[0014]

20 Since the surface layer 4 performs the current collecting function, the negative  
electrode 10 of the present embodiment can have an output terminal 9 attached to the  
surface of the electrode at the position corresponding to the position, in viewing along  
thickness direction of the negative electrode, where the active material layer 3 is located.  
Therefore, it is no more necessary to form an active material-deficient part that has been  
25 required to afford a place where to attach an output terminal. As a result, the negative  
electrode 10 of the present embodiment has an increased capacity compared with  
conventional electrodes. No need to provide an active material-deficient part allows  
the active material layer 3 to be formed continuously, which brings about simplification  
of the production process. The place where to attach the output terminal 9 is not  
30 limited. The output terminal 9 can be directly attached anywhere on the surface of the  
negative electrode 10. This also permits simplification of the production process.  
The structure of the negative electrode 10 according to the present embodiment is  
particularly advantageous where in using a semiconductive, poorly electron-conductive  
material, such as a silicone material, as an active material.

[0015]

In the present embodiment, the negative electrode 10 has the active material layer 3 covered with the surface layers 4 and has the output terminal 9 attached to the surface layer 4. Therefore, the particulate active material 2 is protected from falling  
5 off the active material layer 3 against an outer force that is imposed in attaching the output terminal 9 to the surface layer 4. Methods for attaching the output terminal 9 include ultrasonic welding, laser welding, solder welding, and resistance welding.

[0016]

Each of the surface layers 4 is thinner than a thick conductor used as a current  
10 collector in conventional electrodes. Specifically, the thickness of the surface layer 4 is preferably as small as about 0.3 to 10  $\mu\text{m}$ , still preferably about 1 to 5  $\mu\text{m}$ . Substantially continuous coating of the active material layer 3 can be achieved with this minimum thickness of the surface layers 4. Fall-off of the particulate active material 2 can thus be prevented. The surface layers 4 having a small thickness within the recited  
15 range are preferably formed by electroplating as described later. The two surface layers 4 may be the same or different in thickness.

[0017]

As illustrated in Fig. 1, the negative electrode 10 has a large number of micropores 5 open on at least one of the first surface 1 and the second surface and  
20 leading to the active material layer 3. The micropores 5 are formed in the surface layer 4, extending in the thickness direction of the surface layer 4. The micropores 5 allow a nonaqueous electrolyte to sufficiently penetrate into the active material layer 3 and to sufficiently react with the active material particles 2. In a cross-section of the surface layer 4, the micropores 5 have a width of about 0.1 to 10  $\mu\text{m}$ . The micropores 5 are so  
25 fine and yet wide enough to allow penetration of a nonaqueous electrolyte. In particular, a nonaqueous electrolyte, which has a smaller surface tension than an aqueous one, is capable of penetrating through the micropores 5 with a small width. Such micropores 5 are preferably formed while the surface layer 4 is formed by electroplating.

30 [0018]

The micropores 5 open on the first surface 1 and/or the second surface have an average open area of about 0.1 to 50  $\mu\text{m}^2$ , preferably about 0.1 to 20  $\mu\text{m}^2$ , still preferably about 0.5 to 10  $\mu\text{m}^2$ , in their plan view under an electron microscope. The

average open area in that range assures sufficient penetration of a nonaqueous electrolyte while effectively preventing the particulate active material 2 from falling off. That range also increases the charge/discharge capacity from the initial stage of charge/discharge cycling. To ensure prevention of fall-off of the particulate active material 2, it is preferred that the average open area be 0.1% to 50%, still preferably 0.1% to 20%, of the maximum cross-sectional area of the active material particles 2. The term "maximum cross-sectional area of the active material particles 2" denotes the maximum cross-sectional area of a sphere having a diameter equal to the median diameter ( $D_{50}$ ) of the particles of the particulate active material 2.

10 [0019]

When whichever of the first surface 1 and the second surface satisfies the above average open area range is observed from above under an electron microscope, the ratio of the total open area of the micropores 5 in the microscopic field to the microscopic field area, called an open area ratio, is 0.1% to 20%, preferably 0.5% to 10%, for the same reasons as for the average open area of the micropores 5. For the same reasons, when the first surface 1 or the second surface satisfying the above average open area range is observed from above under an electron microscope, it is preferred for the surface to have 1 to 20,000, still preferably 10 to 1,000, even still preferably 30 to 500, micropores 5 within every 1 cm square field.

20 [0020]

The active material layer 3 interposed between the first surface 1 and the second surface contains particles of the active material 2 having high capability of forming a lithium compound. Such active materials include silicon materials, tin materials, aluminum materials, and germanium materials. Sandwiched in between a pair of the surface layers 4, the active material 2 is effectively protected from falling off due to expansion and contraction associated with charge/discharge cycles. Kept in contact with an electrolyte through the micropores 5, the active material particles 2 are not hindered from participating in the electrode reaction.

[0021]

30 It is preferred to use a silicon material or a tin material as an active material. Particles of the silicon material or tin material include (a) particles of single silicon or single tin, (b) mixed particles containing at least silicon or tin and carbon, (c) mixed particles containing silicon or tin and a metal, (d) particles of a compound of silicon or

tin and a metal, (e) mixed particles containing particles of a compound of silicon or tin and a metal and metal particles, and (f) single silicon or tin particles coated with a metal. Compared with the particles (a), i.e., particles of single silicon or single tin, use of the particles (b) to (f) is advantageous in that pulverization of the silicon material particles  
 5 due to intercalation and deintercalation of lithium is suppressed more: Use of the particles (b) to (f) is also advantageous in that poor electroconductivity of silicon, which is semiconductive, can be compensated for.

[0022]

The maximum particle size of the active material particles 2 is preferably not  
 10 greater than 50  $\mu\text{m}$ , still preferably 20  $\mu\text{m}$  or smaller. The median particle size ( $D_{50}$ ) of the active material particles 2 is preferably 0.1 to 8  $\mu\text{m}$ , still preferably 1 to 5  $\mu\text{m}$ . Particles 2 whose maximum size exceeds 50  $\mu\text{m}$  are apt to fall off to shorten the electrode life. While smaller particles are better with no particular lower limit, a technically practical lower limit of the particle size would be about 0.01  $\mu\text{m}$ . The  
 15 particle size of the particles 2 can be measured by the laser diffraction-scattering method or electron microscopic observation.

[0023]

A too small proportion of the active material in a negative electrode results in insufficient energy density, and the too large proportion tends to cause fall-off of the  
 20 active material. With these tendencies taken into consideration, the proportion of the active material in the negative electrode is preferably 5% to 80%, still preferably 10% to 50%, even still preferably 20% to 50%, by weight.

[0024]

The thickness of the active material layer 3 is adjusted as appropriate to the  
 25 proportion of the active material in the negative electrode and the particle size of the active material. It is not particularly critical in the present embodiment. In general, the thickness is 1 to 100  $\mu\text{m}$ , preferably 3 to 40  $\mu\text{m}$ . The active material layer 3 is preferably formed by applying an electroconductive slurry containing the particulate active material 2 as described infra.

30 [0025]

Taking the electrode's strength and energy density into consideration, the total thickness of the negative electrode 10 inclusive of the surface layers 4 and the active

material layer 3 is preferably about 2 to 50  $\mu\text{m}$ , still preferably about 10 to 50  $\mu\text{m}$ .

[0026]

In the active material layer 3, it is preferred that a material which constitutes the each of the surface layers 4 including the first and the second surface penetrates through the active material layer 3 along the whole thickness direction thereof. The active material particles exist in the material. That is, it is preferred that the active material particles be not practically exposed on the surfaces of the negative electrode but buried in the surface layers 4. Thus, the active material layer 3 exhibits firmer adhesion to the surface layers 4, and the active material is more effectively prevented from falling off. Electroconductivity between the surface layer 4 and the active material is secured by the metal material penetrating through the active material layer 3. Generation of electrically isolated active material particles even in the deep portion of the active material layer 3 are thus prevented effectively. As a result, the current collecting function is retained, reduction in function as a negative electrode is suppressed, and the electrode life is prolonged.

[0027]

It is preferred that the material which constitutes the surface layer 4 penetrates the entire thickness of the active material layer 3 and connects to both of the surface layers 4, whereby the two surface layers 4 are electrically connected via the metal material to provide the negative electrode 10 with increased electroconductivity. That is, the whole negative electrode 10 serves a current collecting function. Whether a metal material having low capability of forming a lithium compound penetrates the entire thickness of the active material layer to connect the two surface layers can be confirmed by electron microscope mapping of distribution of the material. A preferred method of penetrating the material into the active material layer will be described later.

[0028]

It is preferred that the material which constitutes the surface layer 4 does not completely fill the interstices between the active material particles 2 but leave vacant spaces or voids 6 in the active material layer 3. It should be noted that the voids 6 differ from the micropores 5 formed in the surface layer 4. The voids 6 serve to relax the stress caused by expansion and contraction of the active material particles 2 accompanying intercalation/deintercalation of lithium. In this connection, the proportion of the voids 6 in the active material layer 3 is preferably about 5% to 30% by

volume, still preferably about 5% to 9% by volume. The proportion of the voids 6 can be determined by electron microscope mapping. When the active material layer 3 is formed by applying an electroconductive slurry containing the active material particles 2, followed by drying as described infra, voids 6 are necessarily formed in the active material layer 3. Accordingly, the volume proportion of the voids 6 can be controlled within the recited range by properly selecting the particle size of the active material particles 2, the composition of the electroconductive slurry, and the conditions for applying the slurry. The volume proportion of the voids 6 may also be adjusted by pressing the dried active material layer 3 under proper conditions.

10 [0029]

The active material layer 3 preferably contains a particulate electroconductive carbon or metal material 7 in addition to the particulate active material 2, thereby to add improved electroconductivity to the negative electrode 10. From this viewpoint, the amount of the electroconductive carbon or metal material 7 in the active material layer 3 is preferably 0.1% to 20% by weight, still preferably 1% to 10% by weight. The electroconductive carbon material includes particles of acetylene black and graphite. These electroconductive materials preferably have a particle size of 40  $\mu\text{m}$  or smaller, still preferably 20  $\mu\text{m}$  or smaller, in view of imparting more electroconductivity. The lower limit of the particle size is not critical, which means the smaller, the better. In the light of the process of making the particles, the lower limit would be about 0.01  $\mu\text{m}$ .

[0030]

A first preferred process of producing the negative electrode of the first embodiment will be described with reference to Fig. 2. First of all, a negative electrode is made. In the making of a negative electrode, a carrier foil 11 is prepared as shown in Fig. 2(a). The carrier foil 11 is not limited in material but is preferably electrically conductive. As long as being electroconductive, the carrier foil 11 does not need to be metal, but when the carrier foil 11 which is metal is used, such an advantage is obtained that a used foil can be melted and recycled into foil after making the negative electrode. From the standpoint of easy recyclability, the material of the carrier foil 11 is preferably the same as the surface layer 4 formed by electroplating hereinafter described. Serving as a support for making the negative electrode 10, the carrier foil 11 preferably has such strength not to wrinkle or twist during fabrication of the negative electrode. From this perspective, the carrier foil 11 preferably has a thickness of about 10 to 50  $\mu\text{m}$ .

[0031]

The carrier foil can be prepared by, for example, electrolysis or rolling. Rolling provides a carrier foil with small surface roughness. Such a carrier foil with small surface roughness has a merit that a release layer 11a (hereinafter described) is unnecessary. Where the carrier foil 11 is fabricated by electrolysis, on the other hand, operations from production of the carrier foil 11 to production of the negative electrode 10 can be carried out on the same production line. The in-line production of the carrier foil 11 is advantageous for stable production of the negative electrode and reduction of production cost. Electrolytic foil 11 is obtained by electrolysis in an electrolytic bath containing metal ions (e.g., copper or nickel ions) using a rotary drum as a cathode to deposit the metal on the drum. The deposited metal is peeled from the drum to obtain the carrier foil 11.

[0032]

When the carrier foil 11 has small surface roughness, the active material layer 3 can be formed directly on the carrier foil 11. Otherwise, the carrier foil may be provided with a release layer 11a as shown in Fig. 2(a), on which the active material layer 3 is formed. The release layer 11a not only facilitates peeling but imparts anticorrosion to the carrier foil 11. Irrespective of whether or not the release layer 11a is formed, the carrier foil 11 preferably has a surface roughness Ra of 0.01 to 3  $\mu\text{m}$ , still preferably 0.01 to 1  $\mu\text{m}$ , even still preferably 0.01 to 0.2  $\mu\text{m}$ . With this small surface roughness, the electrode directly built up on the carrier foil 11 can be peeled off successfully, or, the release layer 11a can be formed thereon with a uniform thickness. Where the release layer 11a is provided, the surface roughness Ra of the carrier foil 11 may in some cases exceed the recited range without causing any problem; for the surface roughness of the carrier foil 11 would be reduced by the release layer 11a.

[0033]

The release layer 11a is preferably formed by, for example, plating with chromium, nickel or lead or chromating. The release layer 11a may be formed by a mixture of fine particles of copper and a nitrogen-containing compound or a sulfur-containing compound. Such a nitrogen-containing compound and a sulfur-containing compound are disclosed in paragraphs [0037] to [0038] of JP-A-11-317574 and paragraphs [0020] to [0023] of JP-A-2001-140090. It is preferred that the release layer 11a is formed by plating with chromium, nickel or lead or chromating from the viewpoint of good releasing property. The reason for this

preference is that the resulting release layer 11a forms an oxide or salt skin layer, which has a function to reduce the adhesion between the carrier foil 11 and an electrodeposited layer (hereinafter described) thereby to improve releasability. For successful peel, the thickness of the release layer 11a is preferably 0.05 to 3  $\mu\text{m}$ . The release layer 11a formed on the carrier foil 11 preferably has a surface roughness Ra of 0.01 to 3  $\mu\text{m}$ , still preferably 0.01 to 1  $\mu\text{m}$ , even still preferably 0.01 to 0.2  $\mu\text{m}$ , similarly to the carrier foil 11 on which the active material layer 3 is to be formed directly.

[0034]

The carrier foil 11 prepared by electrolysis has, in the nature of the process, a smooth glossy surface on one side thereof and a rough, matte surface on the other side. In other words, the two sides of the electrolytic foil 11 are different in surface roughness. The glossy surface is the side that has faced the rotary drum and the matte surface is the side on which the metal has deposited. The release layer 11a, if necessary, can be formed on either the glossy surface or the matte surface. Forming the release layer 11a on the glossy surface with smaller surface roughness is preferred for better releasability. Where the release layer 11a is formed on the matte surface, it is recommended to use an electrolytic foil formed in the presence of an electrolyte additive, such as the additive disclosed in JP-A-9-143785, or to etch the matte surface before forming the release layer 11a, or to roll the matte surface, thereby to reduce the surface roughness.

[0035]

In the next step, an electroconductive slurry containing active material particles is applied to the release layer 11a to form an active material layer 3 as depicted in Fig. 2(b). Where there is not the release layer 11a, the active material layer 3 is directly formed on the carrier foil 11. The slurry contains a particulate active material, a particulate electroconductive carbon or metal material, a binder, a diluting solvent, etc. Useful binders include polyvinylidene fluoride (PVDF), polyethylene (PE), and an ethylene-propylene-diene monomer (EPDM). Useful diluting solvents include N-methylpyrrolidone and cyclohexane. The slurry preferably contains about 14% to 40% by weight of the particulate active material, about 0.4% to 4% by weight of the particulate electroconductive carbon or metal material, about 0.4% to 4% by weight of the binder, and about 60% to 85% by weight of the diluting solvent.

[0036]

After drying the applied slurry, the carrier foil 11 with the active material layer



3 is then immersed in a plating bath containing a metal material having low capability of forming a lithium compound to conduct electroplating. On immersing the active material layer 3 in the plating bath, the plating bath penetrates into the active material layer 3 and reaches the interface between the active material layer 3 and the release layer 11a. In this state, electroplating is conducted to deposit the metal material having low capability of forming a lithium compound (a) in the inside of the active material layer 3, (b) on the outer surface (the surface in contact with the plating bath) of the active material layer 3, and (c) on the inner surface (the surface in contact with the release layer 11a) of the active material layer 3. As a result, a pair of the surface layers 4 are formed, and the same material as the surface layers 4 penetrates the whole thickness of the active material layer 3 to make the negative electrode 10 shown in Fig. 1 (see Fig. 2(c)).

[0037]

As for the conditions of the electroplating, when, for example, a copper sulfate-based solution is used for plating with copper as a metal material with low capability of forming a lithium compound, recommended conditions are 30 to 100 g/l in copper concentration, 50 to 200 g/l in sulfuric acid concentration, 30 ppm or lower in chlorine concentration, 30° to 80°C in bath temperature, and 1 to 100 A/dm<sup>2</sup> in current density. In using a copper pyrophosphate-based solution, recommended conditions are 2 to 50 g/l in copper concentration, 100 to 700 g/l in potassium pyrophosphate concentration, 30° to 60°C in bath temperature, 8 to 12 in pH, and 1 to 10 A/dm<sup>2</sup> in current density. By appropriately adjusting these electrolysis conditions, the metal material having low capability of forming a lithium compound is allowed to penetrate through the whole thickness of the active material layer 3 to form a pair of surface layers 4 that are electrically connected to each other, and the aforementioned numerous micropores 5 are easily formed in the surface layers 4.

[0038]

The technique of forming the micropores 5 in the surface layer 4 by electroplating does not involve outer force application unlike the hereinafter described method by pressing and is therefore advantageous in that the surface layer 4 is not damaged, which means that the negative electrode 10 is not damaged. The present inventors assume that the micropores 5 are formed during the formation of the surface layer 4 through the following mechanism. Since the active material layer 3 contains the particulate active material 2, it has a microscopically textured surface, that is, a

mixed profile having active sites where deposit grows easily and sites where deposit does not grow easily. When the active material layer 3 having such a surface condition is electroplated, growth of the deposit differs from site to site, and grains of the material making up the surface layer 4 grow into a polycrystalline structure. On further growth of crystals, adjacent crystals meet, resulting in formation of voids in the meeting site. The thus formed voids connect to each other to form the micropores 5. The micropores 5 formed by the above-described method have an extremely fine structure.

[0039]

The micropores 5 can also be formed in the surface layers 4 by pressing the formed electrode 10. In order to obtain sufficient electroconductivity, densification by pressing is preferably such that the total thickness of the active material layer 3 and the surface layers 4 after pressing may be 90% or less, still preferably 80% or less, of that before pressing. Pressing can be carried out with, for example, a roll press. It is preferred that the pressed active material layer 3 still have 5% to 30% by volume of the voids 6 as stated supra. When the active material intercalates lithium and expands volumetrically during charging, the voids 6 serve to relax the stress attributed to the volumetric expansion. Such voids 6 can be obtained by controlling the pressing conditions as described. The void volume of the voids 6 can be determined by electron microscopic mapping as described.

[0040]

In the subject process of production, it is possible to press the active material layer 3 before the electroplating. For the sake of distinguishing from the above-mentioned pressing, the pressing before the electroplating will be called prepressing. Prepressing is effective in preventing separation between the active material layer 3 and the surface layer 4 and preventing the active material particles 2 from being exposed on the surface of the negative electrode 10. Deterioration of battery cycle life due to fall-off of the active material particles 2 can thus be averted. Moreover, prepressing is effective in controlling the degree of penetration of the material constituting the surface layer 4 into the active material 3. Specifically, a high degree of pressing results in reduction of the distance between active material particles 2, which makes the active material 3 less permeable to the material constituting the surface layer 4. Conversely, when the degree of pressing is small, the distance between the active material particles 2 remains long and ready to allow the material making up the surface layer 4 to penetrate into the active material 3. The prepressing

conditions are preferably such that the thickness of the active material layer 3 after prepressing is 95% or less, still preferably 90% or less, of that before prepressing.

[0041]

5 The negative electrode 10 is then separated from the carrier foil 11 at the release layer 11a as shown in Fig. 2(d). While Fig. 2(d) shows that the release layer 11a is left on the side of the carrier foil 11, the release layer 11a is, in fact, left sometimes on the side of the carrier foil 11, sometimes on the side of the negative electrode 10, and sometimes on both. In any case, the presence of the release layer 11a, being extremely thin, gives no adverse influences on the performance of the resulting  
10 negative electrode 10.

[0042]

Finally, an output terminal is attached to either of the surface layers 4 by a prescribed means. As previously stated, methods of attachment include ultrasonic welding, laser welding, and solder welding. The production process of the present  
15 invention does not require positioning the output terminal in an active material-deficient part, as has been needed in attaching an output terminal in the conventional manufacture of electrodes. Therefore, the process of the invention is a simplified process.

[0043]

20 A second and a third preferred process of producing the negative electrode of the present embodiment will then be described only with reference to the points different from the first process. The description about the first process appropriately applies to those particulars of the second and third processes that are not explained here.

[0044]

25 In the second process, one surface of a carrier foil, with or without a release layer formed thereon, is electroplated to form a first surface layer. An electroconductive slurry containing a particular active material is applied to the first surface layer to form an active material layer. The active material layer is electroplated to form a second surface layer. The carrier foil is peeled off the first surface layer to obtain a negative electrode. Thereafter, the same procedure as in the  
30 first process is followed, and two negative electrodes are joined together.

[0045]

The second process is different from the first one in that formation of an active material layer is preceded by formation of one of the surface layers (a first surface layer) on one side of the carrier foil. The subsequent operations are virtually the same as in the first process. The electroplating conditions for the formation of the first surface layer can be the same as those used in the first process, whereby micropores are successfully formed in the first surface layer.

[0046]

In the third process, the formation of the first surface layer on one surface of a carrier foil in the second process is preceded by formation of a thin coat of a material different from the material making the first surface layer. The first surface layer is then deposited thereon by electroplating. The above operation makes it easier to control the number and open area of the micropores to be formed in the first surface layer.

[0047]

The coat serves to make the carrier foil surface, on which the surface layer is to be formed, non-uniform in electroconductivity thereby to form a large number of micropores in the resulting surface layer. The coat is preferably applied to a thickness of 0.001 to 1  $\mu\text{m}$ , still preferably 0.002 to 0.5  $\mu\text{m}$ , even more preferably 0.005 to 0.2  $\mu\text{m}$ . Applied to a thickness in that range, the coat covers the surface of the carrier foil discontinuously, for example in the form of islands.

[0048]

The coat is made of a material different from the material making up the surface layer, whereby the surface layer can successfully be peeled from the carrier foil in the step of peeling. It is preferred that the material of the coat, which is different from the material making the surface layer, contain at least one element of Cu, Ni, Co, Mn, Fe, Cr, Sn, Zn, In, Ag, Au, C, Al, Si, Ti, and Pd.

[0049]

The process of forming the coat is not particularly restricted. For example, the process of forming the coat is selected in relation to the process of forming the surface layer. More specifically, where the surface layer is to be formed by electroplating, it is preferred to form the coat also by electroplating from the standpoint of production efficiency and the like. The coat may also be formed by other processes,

such as electroless plating, sputtering, physical vapor deposition (PVD), chemical vapor deposition (CVD), a sol-gel process, and ion plating.

[0050]

Where the coat is formed by electroplating, a proper plating bath and plating  
 5 conditions are decided according to the constituent material of the coat. For instance, in making the coat of tin, a plating bath having the composition shown below or a tin borofluoride bath can be used. In using these plating baths, the bath temperature is preferably about 15° to 30°C, and the current density is preferably about 0.5 to 10 A/dm<sup>2</sup>.

10	SnSO <sub>4</sub>	30 to 70 g/l
	H <sub>2</sub> SO <sub>4</sub>	60 to 150 g/l
	Cresolsulfonic acid	70 to 100 g/l

[0051]

As stated above, the coat is used to provide the surface, on which a surface  
 15 layer is to be formed, with non-uniform electroconductivity. When the material making the coat is largely different from the carrier foil in electroconductivity, application of the coat immediately imparts non-uniformity of electroconductivity to the surface on which a surface layer is to be formed. Use of carbon as a material of the coat is an example of that case. On the other hand, when the coat is formed of a  
 20 material whose electroconductivity is about the same as that of the carrier foil, such as various metallic materials including tin, application of the coat does not immediately result in non-uniform electroconductivity of the surface for forming a surface layer. Then, in case where the coat is made of such a material, it is preferred that the carrier foil having the coat formed thereon be exposed to an oxygen-containing atmosphere,  
 25 such as the air, in a dried state, thereby to oxidize the surface of the coat (and the exposed area of the carrier foil). By this operation, the surface of the carrier foil on which to form a surface layer takes on nonuniform electroconductivity. When electroplating (described infra) is performed on the surface with the thus created nonuniformity of electroconductivity, there is produced a difference in electrodeposition  
 30 rate between the surface of the coat and the exposed area of the carrier foil. As a result, a surface layer having micropores can easily be formed. The degree of oxidation is not critical in the present invention. According to the present inventors' study, it has been confirmed that allowing the carrier foil having the coat formed thereon in the atmosphere for about 10 to 30 minutes is sufficient. The carrier foil having the coat

formed thereon cannot be protected from being forcibly oxidized, nevertheless.

[0052]

The reason why the exposure of the carrier foil having the coat formed thereon to an oxygen-containing atmosphere is carried out in a dried state is for the sake of oxidation efficiency. Where the coat is formed by electroplating, for example, the carrier foil taken out of the plating bath is dried by means of a dryer, etc. and allowed to stand in the atmosphere for a predetermined time. Where the coat is formed by dry processes, such as sputtering and various vacuum deposition techniques, the drying operation is unnecessary, and the foil having the coat deposited thereon is left to stand in the atmosphere as it is.

[0053]

Oxidizing the coat may be followed by applying a release agent. A surface layer-forming material is deposited by electroplating on the coat, with or without the release agent applied thereon, to form a surface layer. The resulting surface layer contains a great number of micropores attributed to the coat. The plating bath and plating conditions are chosen as appropriate to the material of the surface layer. In making a surface layer of Ni, for instance, a Watts bath having the composition shown below or a sulfamic acid bath can be used as a plating bath. In using these baths, the bath temperature is preferably about 40° to 70°C, and the current density is preferably about 0.5 to 20 A/dm<sup>2</sup>.

NiSO <sub>4</sub> ·6H <sub>2</sub> O	150 to 300 g/l
NiCl <sub>2</sub> ·6H <sub>2</sub> O	30 to 60 g/l
H <sub>3</sub> BO <sub>3</sub>	30 to 40 g/l

[0054]

After forming the surface layer on the carrier foil, the same procedures as in the second process are followed to obtain a negative electrode.

[0055]

The thus obtained negative electrode 10 according to the present embodiment is assembled into a nonaqueous electrolyte secondary battery together with a known positive electrode, separator, and nonaqueous electrolyte. A positive electrode is produced by applying a positive electrode active material mixture to a current collector, drying, rolling, pressing, and cutting or punching. The positive electrode active

material mixture is prepared by suspending a positive electrode active material and, if needed, an electroconductive material and a binder in an appropriate solvent. The positive electrode active material includes conventionally known ones, such as lithium-nickel complex oxide, lithium-manganese complex oxide, and lithium-cobalt complex oxide. Preferred separators include nonwoven fabric of synthetic resins and a porous film of polyethylene or polypropylene. The nonaqueous electrolyte used in a lithium secondary battery, for instance, is a solution of a lithium salt, a supporting electrolyte, in an organic solvent. The lithium salt includes  $\text{LiClO}_4$ ,  $\text{LiAlCl}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiSCN}$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{LiI}$ ,  $\text{LiCF}_3\text{SO}_3$ , and  $\text{LiC}_4\text{F}_9\text{SO}_3$ .

[0056]

The second embodiment of the electrode according to the present invention will then be described by referring to Fig. 3. The second embodiment will be described only with reference to the differences from the first embodiment. The detailed description of the first embodiment applies appropriately to the points of the second one that are not referred to here. The members in Fig. 3 which are the same as in Fig. 1 are given the same reference numerals as used in Fig. 1.

[0057]

As shown in Fig. 3, the negative electrode of the second embodiment has an electroconductive metal foil layer 8 as a core in the middle of its thickness. An active material layer 3 is formed on each side of the metal foil layer 8, and the active material layers 3 are covered with the respective current collecting surface layers 4a and 4b.

[0058]

In each of the active material layers 3, a material which constitutes the surface layers 4a, 4b penetrates through each active material layers 3 along the thickness direction thereof. The active material particles 2 are not exposed on the surface of the electrode and embedded inside the surface layers 4a and 4b. The material which constitutes the surface layers 4a, 4b penetrates the whole thickness of the active material layers 3 and reach the metal foil layer 8. Therefore, the surface layers 4a and 4b electrically connect to the metal foil layer 8 to increase the electroconductivity of the negative electrode as a whole. Similarly to the negative electrode of the first embodiment, the negative electrode of the present embodiment performs a current collecting function as a whole.

[0059]

The negative electrode 10 has an output terminal 9 attached to the surface of the surface layer 4b. Similarly to the first embodiment, the position of attaching the output terminal 9 is at the position corresponding to the position, in viewing along the thickness direction of the negative electrode 10, where the active material layer 3 exists. With the output terminal 9 so attached, the negative electrode of the present embodiment produces the same effects as with the negative electrode of the first embodiment.

[0060]

The surface layers 4a and 4b and active material layers 3 in the present embodiment can be designed to have the same thicknesses as in the first embodiment. For securing increased energy density by minimizing the total thickness of the negative electrode, the thickness of the metal foil layer 8 is preferably 5 to 40  $\mu\text{m}$ , still preferably 10 to 20  $\mu\text{m}$ . From the same viewpoint, the total thickness of the negative electrode is preferably 10 to 100  $\mu\text{m}$ , still preferably 20 to 60  $\mu\text{m}$ .

[0061]

A process for producing the negative electrode according to the present embodiment is briefly described below. An electroconductive slurry containing a particulate active material is applied to both sides of a metal foil layer 8 to form active material layers. The metal foil layer 8 may be previously produced or be produced in an in-line step of the production of the negative electrode. Where the metal foil layer 8 is in-line produced, it is preferably produced by electrolytic deposition. After the applied slurry dries to form active material layers, the metal foil layer 8 having the active material layers thereon is immersed in a plating bath containing a metal material having low capability of forming a lithium compound and electroplated in this state with the metal material to form the surface layers 4a and 4b. By this process a large number of micropores can easily be formed in the surface layers 4a and 4b, and the metal material making the surface layers 4a and 4b penetrates the whole thickness of the active material layers to provide an electrical connection between both the surface layers and the metal foil layer 8.

[0062]

The present invention is not limited to the aforementioned embodiments. For example, while the above embodiments have been described with particular reference to



a negative electrode for nonaqueous electrolyte secondary batteries, the present invention is also applicable to a positive electrode for the same type of batteries.

[0063]

While in the aforementioned embodiments, in the negative electrode, the material which constitutes the surface layer penetrates the entire thickness of the active material layer to electrically connect the two surface layers, the surface layers do not always need to have an electrical connection as long as the current collecting capabilities of each surface layer 4 can be secured sufficiently.

[Brief Description of the Drawings]

10 [0064]

[Fig. 1] Fig. 1 schematically illustrates an enlarged essential part of a first embodiment of the electrode according to the invention.

[Fig. 2] Fig. 2(a), Fig. 2(b), Fig. 2(c), and Fig. 2(d) each illustrate a step of a preferred process for producing an embodiment of a negative electrode according to the invention.

15 [Fig. 3] Fig. 3 schematically illustrates an enlarged essential part of a second embodiment of the electrode according to the invention.

[Fig. 4] Fig. 4 schematically illustrates the structure of a conventional electrode.

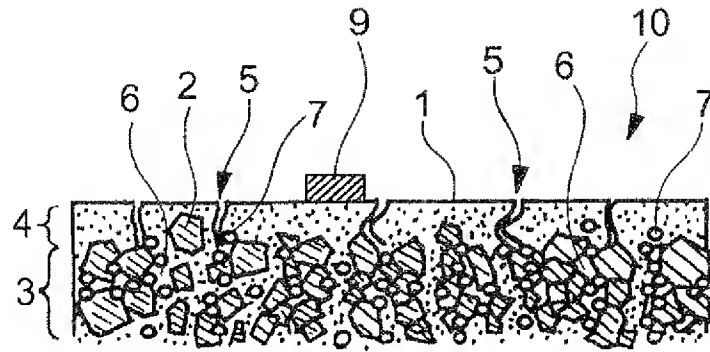
[Reference Numerals]

[0065]

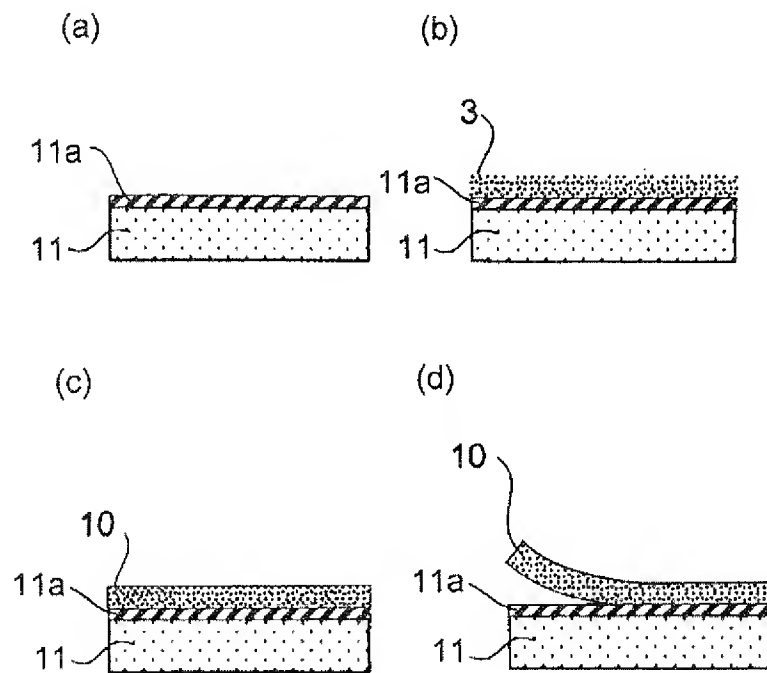
20	1	a first surface
	2	active material particle
	3	active material layer
	4	surface layer
	5	micropore
25	6	void
	7	particulate electroconductive carbon or metal material
	8	metal foil layer
	9	output terminal
	10	negative electrode
30	11	carrier foil
	11a	release layer

[Document Name] DRAWINGS

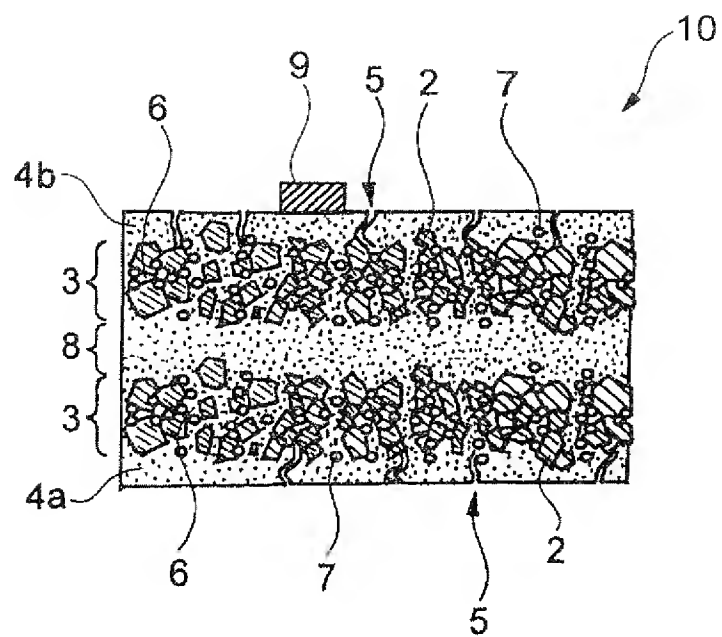
[Fig. 1]



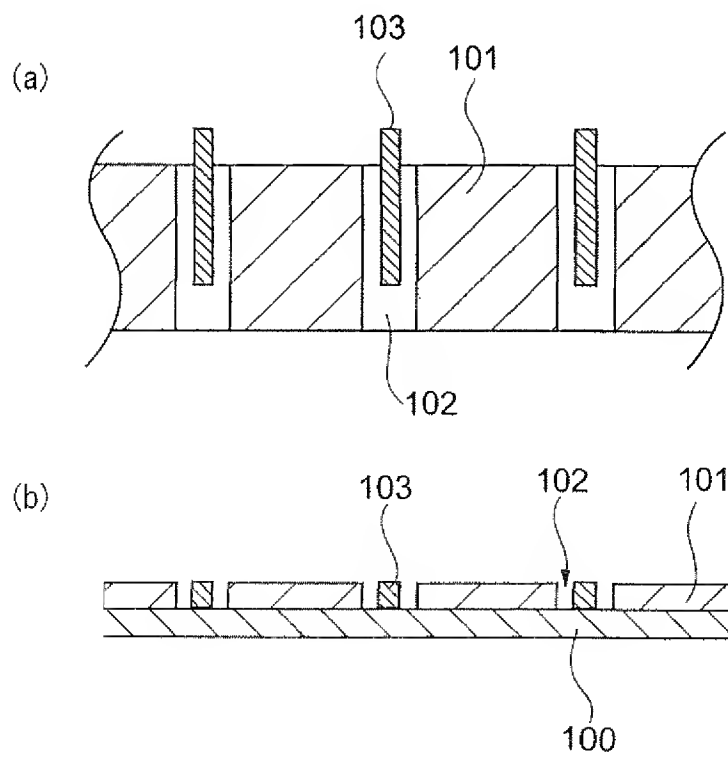
[Fig. 2]



[Fig. 3]



[Fig. 4]



[Document Name]        ABSTRACT

[Abstract]

[Technical Problem]        To provide an electrode for nonaqueous electrolyte secondary  
batteries which has an accordingly increased capacity compared with conventional  
5 electrodes, and brings about simplification of the production process.

[Solution to Problem]        An electrode 10 has an output terminal 9 attached to the  
surface thereof in a region where an active material layer 3 exists in the electrode  
thickness direction. The active material in the active material layer 3 is preferably a  
material having low electroconductivity. The electrode 10 preferably has a pair of  
10 current collecting surface layers 4 that are to come into contact with an electrolyte and  
at least one active material layer 3 interposed between the surface layers 4, the active  
material layer containing a particulate active material 2 having high capability of  
forming a lithium compound.

[Elected Drawing]        Figure 1